

Performance Parameters Of TiN Electrodes For AMTEC Cells

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Abstract. In order to model the lifetime of the electrochemical cell in an Alkali Metal Thermal to Electric Converter (AMTEC), studies of TiN electrodes on beta"-alumina solid electrolytes (BASE) have been made to determine the performance parameters over time. Performance parameters include, G , the morphology factor, and B , the temperature independent exchange current. The results of several experiments, both AMTEC cells and Sodium Exposure Test Cells, in which TiN electrodes have been studied at 1120 - 1200 K are described here.

INTRODUCTION

AMTEC, the Alkali Metal Thermal to Electric Converter, is a direct energy conversion device capable of high efficiencies; it has been demonstrated to perform at high power densities, with open circuit voltages in single electrochemical cells up to 1.6 V and current densities up to 2.0 A/cm² (Weber, 1974; Cole, 1983). As a power system, AMTEC is expected to deliver 20-25 W/kg. The work described in this paper is part of a study to determine the suitability of AMTEC power conversion in NASA's X2000 spacecraft program for exploration of the Solar System's outer planets.

An AMTEC converter must have a lifetime of 5-7 years to provide power for a mission to Europa and 13-15 years to provide power for a mission to Pluto. Lifetime is defined as the time in which the converter power output will degrade to a pre-determined level; this level is set by mission requirements. Previous work on modeling the lifetime of AMTEC cells has focused on the electrode, as it is the component most likely to degrade with time. That work included Mo, Rh_xW (1< x <3), and Pt_xW (1< x <4) electrodes (Ryan *et al.*, 1994). The work presented here has been done in an effort to extend our previous work in electrode life modeling to include TiN electrodes.

The understanding developed in the experiments described here will be used to determine acceleration factors for accelerated operation of AMTEC components. Accelerated operation will allow prediction of the lifetime and possible failure mechanisms of AMTEC cells.

TiN ELECTRODE STUDIES

Titanium nitride electrodes have been extensively tested in AMTEC cells, and have shown relatively high power densities and performance (Asakami *et al.*, 1990 and Sievers *et al.*, 1993). A particular advantage of TiN electrodes has been presumed to be its slow grain growth and stability toward reaction and material migration, and therefore its potential for use in long-lived devices. There are two types of TiN formulations used in state-of-the-art AMTECs. Reactively sputtered TiN electrodes are used on the low pressure side of BASE as cathodes, and "Weber process" electrodes are used on the high pressure side as anodes. "Weber process" electrodes are made by a variation on a reactive nitridation process of a titanium hydride slurry (Weber patent citation). Sputtered TiN electrodes have been operated for relatively short times (up to 150 hours) in liquid anode AMTEC cells at JPL, and for longer periods (up to

1400 hours) in Sodium Exposure Test Cells (SETC).

The SETC is a testing apparatus which allows the operation of electrode materials as two electrode cells in sodium vapor atmosphere. It is not a power producing cell, as the electrodes are held in the same pressure of sodium vapor. Electrodes are deposited on BASE and contacted as they would be in an AMTEC cell, but are operated as electrochemical cells, generally potentiostatically. These cells are not power-producing, but potentiostatic operation allows extraction of electrode and electrolyte performance parameters from current vs. voltage measurements and from Electrochemical Impedance Spectroscopy (EIS). It is a relatively simple setup which allows electrode testing without mounting an entire AMTEC experiment, and has been described in detail elsewhere (Ryan *et al.*, 1993, 1998).

The electrode performance parameters to be discussed here are G, the morphology factor, and B, the temperature independent exchange current. These parameters allow comparison of different formulations of TiN electrodes, of different electrode operating temperatures, and of different experimental set-ups.

G and B have been defined in earlier papers (Williams, *et al.*, 1990a & b). G is defined a geometric factor, but is generally used to describe the impedance to sodium transport in an AMTEC electrode. It is not necessarily dependent on physical pore size; thus it is possible that an electrode that appears dense will have a low G (low impedance to sodium transport from the interface to the vapor space) because sodium transport in that electrode proceeds by mechanisms such as grain boundary diffusion. G is a dimensionless number. B is a factor which allows comparison of the exchange current at the electrode/electrolyte interface at different electrode operating temperatures; it is the exchange current normalized for kinetic components resulting from electrode temperature. The units on B are $\text{AK}^{1/2}\text{m}^{-2}\text{Pa}^{-1}$.

EXPERIMENTAL

Data from four different experiments are presented here.

Experiment 1 was a liquid anode AMTEC experiment, in which reactively sputtered TiN electrodes were operated for 150 hours at 1025 - 1200 K. G and B were calculated for that electrode from EIS.

Experiment 2 was an SETC experiment in which two different preparations of reactively sputtered TiN were operated for 600 hours at 1120 K. G and B were calculated from iV curves and from EIS, respectively.

Experiment 3 was an SETC experiment in which sputtered and Weber TiN samples were operated for 950 hours at 1120 K. G and B were calculated from iV curves and from EIS, respectively.

Experiment 4 was an SETC experiment in which sputtered and Weber TiN samples were operated for 1400 hours at 1170 K. G and B were calculated from iV curves and from EIS, respectively.

The electrodes in Experiment 1 were Weber process electrodes prepared at Ceramatec, Inc. by Neill Weber. One set of electrodes in Experiment 2 was sputtered at JPL, the other was provided by Advanced Modular Power Systems, Inc. (AMPS). There was no measurable difference in performance between the electrodes made at JPL and those provided by AMPS. Both sputtered and Weber electrodes provided by AMPS were operated in Experiments 3 and 4.

In the cases of Experiments 1 and 2, there was no liner in the containment to prevent volatile components from stainless steel from reaching the electrochemical cell (BASE + electrodes). For Experiment 1, which was a liquid anode AMTEC experiment, the stainless steel temperature did not exceed 650 K, so the vapor pressure of the most volatile component, Mn, was not high enough to provide contaminants to the electrode. In Experiment 2, the vapor pressure of Mn, and possibly Cr, was high enough to contaminate the electrodes, so data have been used only up to the point where the electrochemical behavior of the electrodes showed evidence of contamination. There was a fifth experiment, an SETC experiment in which sputtered and Weber TiN samples were operated for 600 hours at 1220 K. Interpretation of the data in that experiment has been difficult because the sodium temperature was not

well known and because the titanium liner in the SETC reacted with Ni in the stainless steel container, resulting in contamination of the electrodes with volatile components in the stainless steel. Data from that experiment are not presented here.

The values computed for B and G in SETC experiments are not known precisely. One factor which is required for calculation of B is the temperature of the liquid sodium (condenser temperature in an AMTEC cell, sodium pool temperature in an SETC). This temperature is not always well known in an SETC because the sodium may wick up the containment, and thus there may be liquid sodium at a temperature somewhat higher than is reported by the temperature of the sodium pool. Non uniform current distribution over the electrode also introduces a correction which is difficult to calculate exactly. However the relative time dependence of the derived values should not be affected by these corrections. A higher sodium temperature will result in a decreased value of B, so the value reported here may be considered to be an approximate upper bound on B in an SETC. G values can only be calculated when current limiting behavior is well defined in the experiment.

RESULTS AND DISCUSSION

Table 1: B and G for four experiments with TiN.

Exp. No.	T _{el} K	B AK ^{1/2} m ⁻² Pa ⁻¹	G	comment
1 el A	1150	40	100	iV curves; heat shields in cell
1 el B	1150	60	100	iV curves; heat shields in cell
1 el B	1150	60	150	EIS
2 (9/93) sputtered	1123	60	50	iV curves/EIS
3 (9/97) sputtered Weber	1130	50 20	60 na	iV curves/EIS
4 (9/98) sputtered Weber	1180	60 15	10 na	iV curves/EIS

Table 1 shows the calculated average values of G and B during the first 150 hours for each of the four experiments, including both Weber and sputtered electrodes, where appropriate. Values of G in Experiment 1 are high, above 100, because the cell was fitted with a heat shield that provided sodium back pressure and inflated the value of G to a value above that which would be caused by electrode performance alone. Those values for G should not be considered as representative of electrode performance in a cell without heat shields. In Experiment 2, the two different formulations of sputtered TiN performed equivalently, so only one value for each electrode performance parameter is reported.

In Experiment 3 in the SETC, it was not possible to calculate values for G in Weber electrodes because limiting currents, which are necessary to calculate G, were not reached. These electrodes had quite high sheet resistances and low exchange currents, and lower currents were obtained at maximum and minimum voltages than for the sputtered electrodes, which did show current limiting. Those electrodes appeared flaky before and after operation, which may account for their poor performance and their inability to be driven to limiting behavior at voltages less

than 5.0 V.

The most noticeable pattern in the values reported in Table 1 is that there is very little variation in the values for B and G in sputtered TiN electrodes from one experiment to another. G is generally 40- 50 and B 50-60 for each experiment with sputtered TiN electrodes. Weber electrodes have much smaller values for B, generally around 10 in the beginning of the experiment.

Figure 1 shows time evolution of values for B in two different SETC experiments, Experiments 3 and 4 (1120 and 1170 K). Only data taken at one sodium pressure are presented here, with the sodium pool temperature in Experiment 3 at 570 K and in Experiment 4 at 520 K. There appears to be a slight decline in B over a period of several hundred hours for sputtered electrodes, but a rise in B over the same period for Weber process electrodes. The rise in B for the Weber electrodes is consistent with thick, flaky electrodes slowly re-forming themselves on the BASE surface to make a more intimate contact, and thus a larger reaction zone. In Experiment 3, there was a temperature cycle around 500 hours, and both the sputtered and Weber electrodes show evidence of having delaminated on cool down, and re-adhering over time with high temperature and operation.

We can see from Figure 1 that B is not substantially different for the two experiments, in spite of the difference in operating temperature and in Na pool temperature. There is a decline in the value of B when it is operated at 1170 K for several hundred hours. Developing an understanding and modeling the causes of this drop will allow life modeling and accelerated testing factors to be determined. Operation for 1000 hours at 1120 K did not show substantial decline in the value of B.

The rise in B starting around 500 hours for both sputtered and Weber TiN at 1120 K is attributed to a temperature cycle at 500 hours. We suggest that the electrodes delaminated when cooled, then re-adhered when re heated, returning B to its approximate value before the temperature cycled.

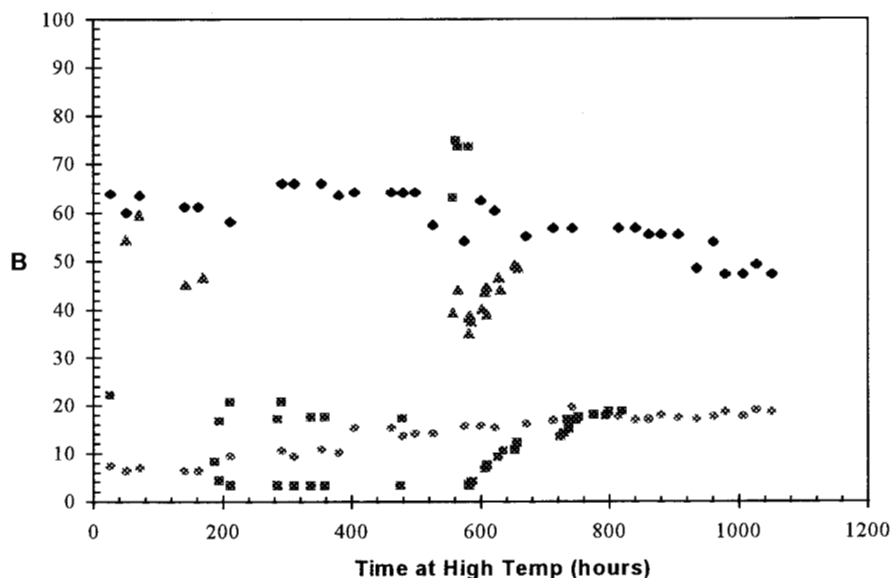


FIGURE 1. Time evolution of B for sputtered and Weber electrodes. Squares and triangles, Weber and sputtered at 1120 K, respectively. Circles and diamonds, Weber and sputtered at 1170 K, respectively.

The time evolution of performance parameters for Weber electrodes are very interesting. In both 1120 K and 1170 K SETC experiments, Weber electrodes improved in performance with time, as seen in the increase in B with time.

This increase in B may be attributed to developing a more intimate contact between the BASE surface and the electrode as the electrode is heated. The improved contact will result in a decrease in the interfacial impedance and an increase in the effective reaction area, with an accompanying increase in the exchange current. In any case, the overall performance of an AMTEC cell will be much more strongly dependent on the performance of the cathode than on that of the anode, as losses in the BASE and at the cathode/electrolyte interface will determine the extent of reaction, so improvement in the performance of the anode will probably not be reflected in overall performance of an AMTEC cell.

CONCLUSIONS

In a series of experiments conducted to study the electrode performance of TiN electrodes for AMTEC cells, the performance parameters B, the temperature independent exchange current, and G, the morphology factor, have been calculated. The values for these parameters have been fairly uniform, with B generally 40 - 60 and G around 50. Some preparations of sputtered TiN have smaller G, indicating better sodium transport, but as yet no reason for the difference has been found. As of this writing, Experiment 4 is still operating, and so final evaluation of the electrode performance is not yet complete.

There is a slight drop in B for sputtered electrodes during the first thousand hours of operation; the drop is greater at higher temperature, 1170 K. There may not be such a drop at 1120 K, indicating the possibility that TiN will be a long-lived electrode if operated at 1120 K. Both sputtered and Weber process electrodes show "healing" behavior after a temperature cycle: the electrode performance drops after cycling, presumably because of delamination, and upon reheating, the electrode performance slowly returns to its previous point. This characteristic leads to the conclusion that TiN is a rugged electrode that can resist temperature cycling by self-repair.

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